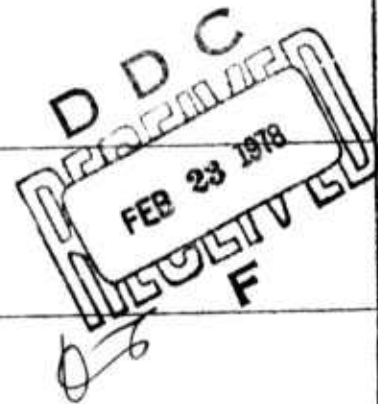


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have been used to measure the variation of the chemical potential and diffusivity of lithium (sodium) with composition x in Li_xTaS_2 (Na_xTaS_2). Such thermodynamic and kinetic data are necessary not only to understand chemical bonding and transport mechanisms in these materials but also to quantitatively assess their specific applications as high energy-density electrodes in alkali-metal battery systems. The sodium diffusivity in Na_xTaS_2 is greater than $10^{-8} \text{ cm}^2/\text{sec}$ when x is between 0.1 and 0.7, which is extraordinarily high for a solid at room temperature. A model which explains the observed variation of sodium diffusivity with composition x in Na_xTaS_2 has been postulated.

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High Energy - Density Electrodes for Alkali-Metal
Battery Systems

AFOSR Grant 77-3319 (April 1, 1977-July 31, 1977)

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Final Scientific Report

The transition - metal disulfides have received considerable attention in recent years because of their potential applications as cathodes in alkali-metal secondary batteries. These disulfides (i. e., TaS_2) have layered structures in which a van der Waals gap exists between adjacent sulfur layers. Alkali metals such as lithium and sodium are easily intercalated in this gap at ambient temperatures. These intercalated compounds have the chemical formula Li_xTaS_2 or Na_xTaS_2 , where x can vary from 0 to 1.0.

The objective of our research program is to determine the fundamental thermodynamic and kinetic information necessary to assess the potential applications of these compounds as cathode materials in secondary batteries. For example, knowledge of the variation of the thermodynamic voltage and the diffusivity of lithium and sodium with composition, x, in these compounds is required to calculate operating voltages and reversibility characteristics of real battery systems.

In our laboratory, techniques for preparing well-characterized intercalated Li_xTaS_2 and Na_xTaS_2 have been developed. Heating in excess

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sulfur at $\sim 500^{\circ}\text{C}$ is essential to remove excess tantalum atoms in the van-der-Waals layers of the commercially prepared TaS_2 . The excess tantalum atoms strongly inhibit the intercalation process by decreasing mobilities of the alkali metals in the van-der-Waals layers.

The thermodynamic and kinetic properties of these intercalated compounds have been determined using cell (I) in which a pure alkali metal A is the anode and the intercalated A_xTaS_2 compound is the cathode.



Propylene carbonate electrolytes have been used in our ambient temperature studies. We have used Na_xTaS_2 and Li_xTaS_2 electrodes in our initial experiments, because the known structural and electrical properties of TaS_2 indicate that intercalated TaS_2 should be an excellent reversible cathode.

The open-circuit thermodynamic voltage of cells using a Li_xTaS_2 cathode and a pure lithium anode varies linearly with x at 27°C . The voltage decreases from 2.92 to 1.46 volts as x in Li_xTaS_2 increases from 0 to 1.0.

Similar electrochemical cell measurements have been made using Na_xTaS_2 cathodes. The thermodynamic cell voltage at 27°C is also a linear function of the sodium content, x , in Na_xTaS_2 . The voltage decreases 2.72 to 0.94 volts as x increases from 0 to 1.0.

The chemical diffusivity of sodium in Na_xTaS_2 at 27°C has been measured using current-pulse techniques. A current pulse is applied

to cell (I) and a known excess of the alkali metal is deposited at the electrolyte - Na_xTaS_2 interface. With small changes in cell voltage, the diffusivity of the alkali metal in Na_xTaS_2 can be determined from measurements of the transient voltage. The diffusivity of sodium in Na_xTaS_2 is greater than $10^{-8} \text{ cm}^2/\text{sec}$ when x is between 0.1 and 0.7, which is extraordinarily high for a solid at room temperature. A model which explains the observed variation of the sodium diffusivity with composition x in Na_xTaS_2 has been postulated.

The experimental details and results of our studies are described in detail in the two enclosed reprints which will be published in Electrode Materials and Processes for Energy Conversion and Storage.

To appear in "Electrode Materials and Processes for Energy Conversion and Storage", J. D. E. McIntyre, S. Srinivasan and F. G. Will eds., The Electrochemical Society, Princeton, N. J. (1977).

ELECTROCHEMICAL DETERMINATIONS OF THE
CHEMICAL POTENTIAL AND DIFFUSIVITY
OF SODIUM IN Na_xTaS_2 AT 300°K

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One major impediment in the development of secondary alkali-metal battery systems with high energy density is the lack of suitable electrode materials. Dichalcogenides of the Group IV and V transition metals intercalated with lithium or sodium offer exciting possibilities as novel electrodes. Electrochemical cell techniques have been used to measure the variation of the chemical potential and diffusivity of sodium with composition x in Na_xTaS_2 where x varies from 0 to 1.0. The measured cell voltage at 300°K is a linear function of sodium content. The chemical diffusivities of sodium measured by current pulse techniques are greater than $10^{-8} \text{ cm}^2/\text{sec}$.

Introduction

In recent years, there has been an increased interest in the development of ambient temperature alkali-metal reversible batteries. Research has been directed toward solid electrodes that are compatible with the new or existing electrolytes. When considering a prospective electrode material, a list of desired characteristics can be tabulated¹:

Table I

1. High electronic conductivity
2. Wide compositional range
3. Low μ_A in cathode
High μ_A in anode
4. Minimal compositional variation of μ_A
5. High diffusivity of A
(A is the active species of the cell)

The Groups IV and V transition metal dichalcogenides have shown promise as cathode materials in alkali metal batteries²⁻⁶. These transition metal dichalcogenides are extremely interesting

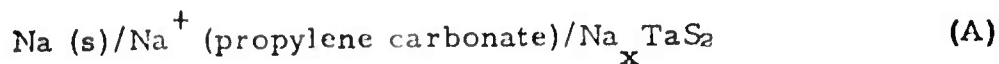
due to their unusual layered crystal structure⁷. Figure 1 shows a schematic picture of the stacking sequence of hexagonally arrayed layers of metal and chalcogen. The metal atoms are in either octahedral or trigonal prismatic coordination. The interesting property of this crystal structure is the existence of one sulfur layer immediately above another sulfur layer giving rise to weak van der Waals bonding between layers. This weak bonding in the dichalcogenides is demonstrated by their marked cleavage properties and the ease with which they are intercalated. The weak bonding between neighboring chalcogen layers manifests itself in numerous polytypic structures, which occur due to different stacking sequences of the hexagonal layers. Tantalum disulfide, for example, has been reported to form 5 polytypes^{7,8} (1T, 2H, 3R, 4H, 6H). Annealing below 450°C or slow cooling results in the formation of the 2H polytype.

The Groups IV and V dichalcogenides are small bandgap semiconductors or metallic conductors⁷. For example, tantalum disulfide has a room temperature resistivity between 10^{-3} to 10^{-4} ohm-cm depending on crystallographic orientation⁹.

Since Rudorff¹⁰ first demonstrated that alkali metals could be intercalated into the van der Waals gaps between layers, the physical and chemical properties of the transition-metal dichalcogenides have been studied by numerous investigators¹⁻²¹. These investigators have shown that the intercalation process is extremely rapid and that crystallographically only the c axis of the dichalcogenide is significantly increased by intercalation; thus indicating that the alkali metals reside in the van der Waals gap between sulfur layers and have a high mobility.

Omloo and Jellinek¹⁸ have studied the crystallography of alkali metal intercalated niobium and tantalum dichalcogenides. These authors proposed several models for the crystallographic structure but were unable to make an unequivocal decision as to which structure applied. They found a non-stoichiometry range for Na_xTaS₂ from $x = 0.4$ to $x = 0.7$, the upper limit being determined by the attack of the quartz capsules by sodium.

Sodium intercalated tantalum disulfide meets the first two criteria in Table I for a solid electrode. The applicability of the remaining three criteria for an ideal solid electrode are assessed. Cell A is used to measure the chemical potential and diffusivity



of sodium in $\text{Na}_x \text{TaS}_2$.

Experimental

Tantalum disulfide was prepared by heating commercial powder (-325 mesh, Cerac/Pure 99.8%) at 850°K with excess sulfur for at least one week. The excess sulfur was used to bring the metal sulfur ratio close to the 1:2 composition. This annealing followed by a slow cool converts all the tantalum disulfide to the 2H-polytype. Combustion of the annealed TaS_2 to Ta_2O_5 gave the chemical stoichiometry $\text{Ta}_{1.01}\text{S}_2$. The existence of only the 2H-polytype was confirmed by X-ray diffraction.

Sodium was intercalated into tantalum disulfide lattice using sodium naphthalide dissolved in tetrahydrofuran²². The sodium naphthalide solution was prepared by mixing equal molar amounts of sodium (ROC/RIC 99.95%) and naphthalene (Aldrich 99 + %) followed by addition of the tetrahydrofuran (THF) solvent to obtain a dark green solution. Weighed powder samples of TaS_2 were added to various concentrations of sodium naphthalide in THF to obtain samples of $\text{Na}_x \text{TaS}_2$ with various values of concentration x . Addition of the powder to the intercalating solutions resulted in a noticeable heating of the solutions. Intercalation was practically complete within 24 hrs. but powders were kept in the solutions three or four days before being filtered and washed with THF. Analysis of the sodium naphthalide solutions was performed before and after the intercalation of the TaS_2 powder. The sodium content of the intercalation solutions was determined using the method of Paul, Lipkin and Weissman²², i.e. 50% dilution with water and subsequent titration with HCl. The sodium content of the intercalated disulfides was calculated from the sodium loss of the sodium naphthalide solutions. A small amount of the $\text{Na}_x \text{TaS}_2$ powders was sealed in glass capillaries and used for X-ray^x diffraction studies. The propylene carbonate (Aldrich 99%) used as electrolyte solvent was equilibrated with lithium chips to remove residual moisture and oxygen. Gas chromatographic analysis showed no detectable amounts of these impurities. Sodium salts, NaI (Alfa/Ventron, 99.9) or NaPF_6 (Alfa Ventron 98%), were dried under vacuum at 150°C for 3 or 4 days and then added to the propylene carbonate to obtain a saturated solution.

The experimental cell design is shown in Fig. 2. Intercalated

tantalum disulfide powder was compacted in a 1 cm cylindrical die at 30 ksi (thousand pounds per square inch) to form a cylindrical pellet. The pellet was springloaded between two 304 stainless steel discs, which were suspended in the electrolyte by a 1/8" 304 stainless steel rod which was also the electrical lead to the cathode. The anode was sodium metal compacted into a 304 stainless steel tube suspended into the electrolyte with a 304 stainless steel rod. All cell compartments were tested for leaks with a helium leak detector.

The temperature was maintained within $\pm 0.2^\circ\text{K}$ by a constant temperature bath, and temperature measurement was with a mercury thermometer readable to $\pm 0.05^\circ\text{K}$. The cell voltage was measured by either a Keithley 630 potentiometric electrometer or a Fluke 895A differential voltmeter. Current pulses of 3 to 22 mA/cm² and 2 to 45 seconds were generated using a Tacussel potentiostat.

The handling of all moisture and oxygen sensitive materials was performed in a Vacuum Atmospheres glove box (≈ 1 ppm H₂O). X-ray diffraction studies were performed with either cylindrical Debye-Scherrer cameras or a Phillips diffractometer. All diffraction studies used CuK _{α} radiation.

Results

The measured values of emf as a function of composition x of Na _{x} TaS₂ are shown in Fig. 3. The measured emf can be fitted by a linear function of composition,

$$E = b + mx \equiv 2.72 - 1.78x \quad (1)$$

Application of the Gibbs-Duhem equation to Na-TaS₂ solid solutions for a constant Ta:S ratio gives:

$$d\mu_{\text{TaS}_2} = - \frac{N_{\text{Na}}}{N_{\text{TaS}_2}} d\mu_{\text{Na}} = -x d\mu_{\text{Na}} \quad (2)$$

where x is the composition of Na _{x} TaS₂

$$\text{or } \mu_{\text{TaS}_2} = - \int_{x=0}^x x d\mu_{\text{Na}} = +nF \int_{x=0}^x x dE \quad (3)$$

$$\text{Since } \mu_{\text{Na}} = -nFE$$

It can also be shown that:

$$\Delta G_{\text{Na}_x\text{TaS}_2}^f = x\mu_{\text{Na}} + \mu_{\text{TaS}_2} + \Delta G_{\text{TaS}_2}^f \quad (4)$$

$$= -nF \left[xE \Big|_0^x - \int_0^x x dE \right] + \Delta G_{\text{TaS}_2}^f$$

$$= -nF \int_0^x E dx + \Delta G_{\text{TaS}_2}^f \quad (5)$$

From thermodynamic equilibrium studies by Larson and Elliott²³ of TaS₂ at elevated temperatures a value of -70.5 ± 3 kcal/mole for $\Delta G_{\text{TaS}_2}^f$ at 300°K is obtained. All free energy values quoted in this paper are using sulfur as the standard state. (The difference between solid sulfur and a gaseous sulfur standard state is $+9.5$ kcal/g-atom of sulfur at 300°K). Using -70.5 kcal/mole for $\Delta G_{\text{TaS}_2}^f$, the free energy of formation of NaTaS₂ is calculated from Eq. (5) with $x=1$ to be -112.7 ± 3 kcal/mole.

The diffusivity of sodium in Na_xTaS₂ was measured using a current-pulse relaxation technique.^x In this method, a current pulse is used to approximate an instantaneous source or sink of sodium at the electrolyte-cathode interface. The solution of Fick's second law for an instantaneous planar source²⁴ is

$$C - C_0 = \frac{i\tau}{F(\pi Dt)^{1/2}A} e^{-a^2/4Dt} \quad (6)$$

where C is the composition at any point at any time

C₀ is the initial uniform composition

i is the current of pulse

τ is the duration of the pulse

a is the distance from instantaneous planar source

D is the diffusivity

t is the time

F is Faraday's constant (=96500)

For sodium intercalated tantalum disulfide, the concentration is given by:

$$C_{\text{Na}} = \frac{x}{V} \quad (7)$$

where V is the molar volume

x is the composition parameter of Na_xTaS₂

Combining Eqs. (7), (6) and (1) for $a = 0$

$$\Delta E = \frac{m V i \tau}{F A (\pi D t)^{\frac{1}{2}}} \quad (8)$$

The value of \tilde{D}_{Na} for a specific composition x is derived from the slope of the ΔE vs $t^{-\frac{1}{2}}$ curve obtained for a cathode of that composition. A typical plot of ΔE vs $t^{-\frac{1}{2}}$ is shown in Fig. 4. The compositional variation of the molar volume was obtained from experimentally determined X-ray lattice parameters. The molar volume was found to be between 41 and 42 cm³ for $x \geq 0.05$. The molar volume of pure TaS₂ is 34.6 cm³.

The experimentally measured values of \tilde{D}_{Na} as a function of composition x are shown in Fig. 5. These diffusivity values were obtained using the geometric surface area of the compacted cathode directly in contact with the propylene carbonate electrolyte. The effects of surface roughness and the planar surfaces between the metal discs and cathode (Fig. 2) have not been considered. No variation of \tilde{D}_{Na} within experimental error was observed on changing the thickness of the cathode pellet (changing the cylindrical area but not the planar areas). The error introduced by using a planar diffusion solution for a cylindrical geometry was calculated using a finite differences solution for the cylindrical geometry. The error involved was found to be minimal for the times involved in the experiments and diffusivities measured. Tantalum disulfide crystals grown by vapor transport²⁵ were ≈ 1 nm x 1 mm platelets. These crystals were intercalated and used to make one cathode. The diffusivity measured with this cathode showed no difference within experimental error of the diffusivity of a cathode compacted from intercalated powder.

Discussion

The measured linear dependence of emf on composition suggests that sodium and tantalum disulfide form a single phase solid solution over the entire composition range, even though X-ray analysis shows no apparent change in lattice parameter for $x > 0.3$. Evidently the lattice expansion required to accommodate intercalated sodium occurs rapidly with the insertion of the first few sodium atoms. Omloo and Jellinek¹⁸ did not observe a leveling off of the c parameter until $x > 0.7$.

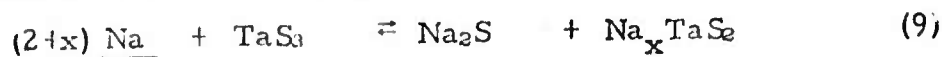
Whittingham² and Winn, Shemilt and Steele⁵ have investigated the thermodynamics of alkali-metal intercalated TiS₂. When TiS₂ is

intercalated with lithium the chemical potential of lithium is a smooth function of composition x in Li_xTiS_2 varying from -58.8 kcal/mole for $x \approx 0$ to -43.12 kcal/mole for $x = 1$ and can be easily fitted by a linear relationship². Basu and Worrell²⁶ investigated lithium intercalated tantalum disulfide and also found that the chemical potential of lithium is well fitted by a linear function of composition x . Winn, et al.⁵ reported that the chemical potential of sodium is independent of disulfide non-stoichiometry in Na_xTiS_2 for values of x less than ≈ 0.45 . Above $x = 0.45$ the chemical potential of sodium is very dependent on the non-stoichiometry of TiS_2 and shows a large change in the slope of the chemical potential-composition curve in making the transition. Leblanc-Soreu, et al.²⁰ reported that X-ray diffraction studies of Na_xTiS_2 showed 3 distinct phases as the composition changed. In comparison, the measurements of Winn, et al. do not lead to an unambiguous conclusion of the existence of a two phase region. The region around $x = 0.425$ could be interpreted as a two phase region. In comparison, the results of this study resemble those of Whittingham² for Li-TiS_2 , and Basu and Worrell for Li-TaS_2 in that Li_xMS_2 appears to be single phase for $0 < x < 1$ and the chemical potential of alkali metal is a linear function of composition x .

The measured values of the chemical potential can be correlated with the stable phases in the Na-Ta-S-ternary system. At 300°K , Na_2S is the only stable phase in the Na-S binary, and no solid solubility or intermetallic phases are reported in the Na-Ta binary²⁷. The Ta-S binary on the other hand has many reported phases, although some studies are in conflict²⁸⁻³¹. The major question is which of the reported phases are equilibrium phases at ambient temperature. The reported phases are Ta_6S , Ta_2S , TaS , $\text{Ta}_{1+y}\text{S}_2$, TaS_2 , and TaS_3 ²⁸⁻³¹. The first two phases could only be formed at temperatures above 1600°C ^{28,29} and are probably unstable at 300°K . Biltz and Kocher³¹ reported the existence of TaS but it was not found by Jellinek³⁰. Tantalum monosulfide is a phase similar to niobium monosulfide which is stable at low temperatures and decomposes above 800°C ³⁰. Jellinek³⁰ may not have observed TaS because his preparation temperatures were above 800°C . The phase $\text{Ta}_{1+y}\text{S}_2$ is similar to TaS_2 in structure with the excess metal atoms occupying positions in the van der Waals gaps between sulfur layers. We assume that the reported $\text{Ta}_{1+y}\text{S}_2$ phase³⁰ is within the non-stoichiometry range of TaS_2 .

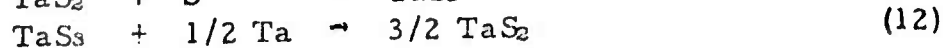
Assuming Na_2S , TaS_3 , TaS_2 and TaS are the only stable binary phases, the isothermal ternary section for Na-Ta-S shown in Fig. 6 has been constructed. The composition of Na_xTaS_2 in the upper

three phase triangle (I) (Na_2S , TaS_3 , Na_xTaS_2) can be determined by considering the following equilibrium:



$$\text{where } (2+x) \mu_{\text{Na}} + \Delta G_{\text{TaS}_3}^f = \Delta G_{\text{Na}_2\text{S}}^f + \Delta G_{\text{Na}_x\text{TaS}_2}^f \quad (10)$$

In order to calculate x in Na_xTaS_2 from Eq. (10) the free energy of formation of TaS_3 must be estimated. Since TaS_3 is a stable phase, the stability of TaS_3 can be estimated from the following reactions at 300°K .



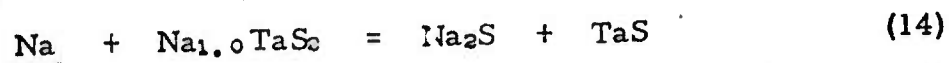
Eqs. (11) and (12) require that $\Delta G_{\text{TaS}_3}^f$ be between -70.5 and -105.75 kcal/mole. Assuming that TaS_3 is only slightly more stable than TaS_2 ³⁰, we estimate a value for $\Delta G_{\text{TaS}_3}^f$ of -75 kcal/mole.

Substituting this estimated value of $\Delta G_{\text{TaS}_3}^f$, the literature value of $\Delta G_{\text{Na}_2\text{S}}^f$ (-86.5 kcal/mole)³² and Eqs. (1) and (5) for μ_{Na} and $\Delta G_{\text{Na}_x\text{TaS}_2}^f$ respectively, into Eq. (10), gives the following equation:

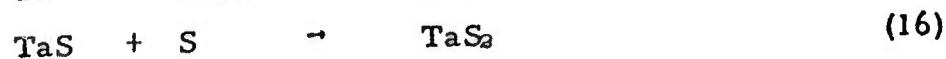
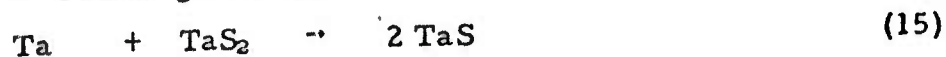
$$20,530 x^2 + 82,090 x - 43,400 = 0 \quad (13)$$

Using Eq. (13), one calculates the composition x in Na_xTaS_2 which is in equilibrium with Na_2S and TaS_3 . As shown in the upper three-phase triangle of Fig. 6, this composition is $\text{Na}_{0.47}\text{TaS}_2$.

The lower three phase triangle (II) in Fig. 6 is represented by



The free energy of formation of TaS calculated from Eq. (14) using the value of $\Delta G_{\text{Na}_2\text{S}}^f$ given above and Eqs. (1) and (5) for $x = 1$ is -47.9 ± 3 kcal/mole. This is close to the value of -50.2 kcal/mole derived by Basu and Worrell²⁸ from the Li-Ta-S ternary. As with TaS_3 , the binary phase diagram can be used to obtain limits on the stability of TaS as given by:



Eqs. (15) and (16) require that ΔG_{TaS}^f be between -35.25 and -70.5 kcal/mole. The calculated value for Eq. (14) is within these limits.

If it is assumed TaS is not stable, a three phase triangle between Na_2S , Na_xTaS_2 and Ta would exist. Such a three phase equilibrium results in a value of -4.74 kcal/mole for μ_{Ta} . Since the solubility of sulfur and sodium in solid tantalum is expected to be low, the chemical potential of tantalum should be essentially zero.

The measured values of \tilde{D}_{Na} show a significant variation for a single composition. Even considering the experimental scatter the values of \tilde{D}_{Na} exhibit a good fit to a curve of the form

$$\tilde{D}_{\text{Na}} = \text{const} [x(1-x)^2] \quad (17)$$

as shown in Fig. 7.

The thermodynamic factor of sodium in the intercalated disulfides $\left(\frac{d \ln a_{\text{Na}}}{d \ln C_{\text{Na}}} \right)$ can be calculated from Eqs. (1) and (7) to give

$$\frac{d \ln a_{\text{Na}}}{d \ln C_{\text{Na}}} = \frac{F}{RT} \frac{d E}{d \ln x/V} = -\frac{F m}{RT} x \quad (18)$$

It is also expected that the diffusivity of sodium will decrease with increasing sodium content within a layer because the number of vacant sites decreases. As shown in Fig. 7, sodium atoms can occupy octahedral or tetrahedral sites in the van der Waals gap between sulfur layers. For a completely ionized sulfur, the octahedral site can accommodate an atom with a radius less than 1.18 \AA . The tetrahedral site can only accommodate an atom with radius less than 0.85 \AA . The ionic radius of sodium is 0.95 \AA . Since the sulfur is not completely ionized the values calculated above are too small and sodium may occupy either site. However, the octahedral site is selected as the favored site because of its relatively larger size. Movement from one octahedral site to another octahedral site involves movement through a tetrahedral site. It is further assumed that a tetrahedral site can not be occupied if any one of the surrounding octahedral sites is filled. This assumption leads to a dependence of diffusivity on the probability of two octahedral sites being empty. Since there is one octahedral site per TaS_2 the probability of an octahedral site being empty is $(1-x)$. Combination of this dependence on site occupation and the thermodynamic factor calculated in Eq. 18 gives the observed variation of \tilde{D}_{Na} with x shown in Eq. (17).

The only other reported study of the diffusivity of alkali-metals

in transition metal dichalcogenides is the work of Winn, et al.⁵ These authors report the diffusivity of sodium in TaS_2 to be approximately $10^{-9} \text{ cm}^2/\text{sec}$ but their data suffers from an error in the analysis³³.

Summary

The existence of a wide compositional range for Na_xTaS_2 has been confirmed ($0 < x < 1$). The chemical potential of sodium in the Na-TaS_2 solid solution changes significantly from -63.42 kcal/mole to -21.6 kcal/mole. The diffusivity of sodium in Na_xTaS_2 is greater than $10^{-9} \text{ cm}^2/\text{sec}$ when x is between 0.05 and 0.9, which is extraordinarily high for a solid at room temperature.

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References

1. W. L. Worrell and A. S. Nagelberg in Proceedings of the Symposium and Workshop on Advanced Battery Research and Design, Argonne National Laboratory, March, 1976, p. B1.
2. M. S. Whittingham, *Science* 192, 1126 (1976).
3. L. H. Gaines, R. W. Francis, G. H. Newman and B. M. L. Rao, Paper at 11th IECEC, p. 418.
4. U. S. Patent 19659W/12 = BE-819-672.
5. D. A. Winn, J. M. Shemilt and B. C. H. Steele, *Mat. Res. Bull.* 11, 559 (1976).
6. G. L. Holleck, F. S. Shuker and S. B. Brummer in Proceedings of the 10th Intersociety Energy Conversion Engineering Conf., Newark, Del., Aug. 1975.
7. J. A. Wilson and A. D. Yoffe, *Adv. in Phys.* 18, 193 (1969).
8. S. F. Meyer, R. E. Howard, G. R. Stewart, J. V. Acrivos and T. H. Geballe, *J. Chem. Phys.* 62 (11) 4411 (1975).

References (continued)

9. A. H. Thompson, F. R. Gamble and R. F. Koehler, Phys. Rev. B5, 2811 (1972).
10. W. Rüdorff, Chimia 19, 489 (1965).
11. F. R. Gamble, J. H. Osieki and F. J. DiSalvo, J. Chem. Phys. 55, 3525 (1971).
12. M. S. Whittingham, Mat. Res. Bull. 9, 1981 (1974).
13. M. S. Whittingham, J. Chem. Soc., Chem. Comm. 328 (1974).
14. G. V. Subba Rao and J. C. Tsang, Mat. Res. Bull. 9, 921 (1974).
15. M. S. Whittingham and A. H. Thompson, J. Chem. Phys. 62, 1588 (1975).
16. M. S. Whittingham and F. R. Gamble, Mat. Res. Bull. 10, 383 (1975).
17. M. B. Dines, Mat. Res. Bull. 10, 287 (1975).
18. W. P. F. A. M. Omloo and F. Jellinek, J. Less-Comm. Metals 20, 121 (1970).
19. R. B. Somoano, V. Hadek and A. Rembaum, J. Chem. Phys. 58, 697 (1973).
20. A. Leblanc-Soreu, M. Danot, L. Trichet and J. Rouxel, Mat. Res. Bull. 9, 191 (1974).
21. R. Schöllhorn and A. Weiss, J. Less-Comm. Metals 36, 229 (1974).
22. D. E. Paul, D. Lipkin and S. J. Weissman, J. Am. Chem. Soc. 78, 116 (1956).
23. H. R. Larson and J. F. Elliott, Trans. TMS-AIME 239, 1713 (1967).
24. J. Crank, Mathematics of Diffusion, Oxford, 1956.

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References (continued)

25. E. Coleman B. S. thesis, Univ. of Pa.
26. S. Basu and W. L. Worrell in the Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage, ECS, 1977.
27. M. Hansen, Constitution of Binary Alloys, McGraw-Hill, New York, 1958, p. 1164.
28. H. F. Franzen and J. G. Smeggil, Acta.Cryst. B25, 1736 (1969).
29. H. F. Franzen and J. G. Smeggil, Acta.Cryst. B26, 125 (1970).
30. F. Jellinek, Arkiv. fur Kemi. 20 (36), 447 (1963).
31. W. Biltz and A. Köcher, Z. Anorg. allg. Chem. 248, 172 (1941).
32. JANAF Thermochemical Tables, ed., D. R. Stull and H. Prophet, 1971.
33. Private Communication, B. C. H. Steele.

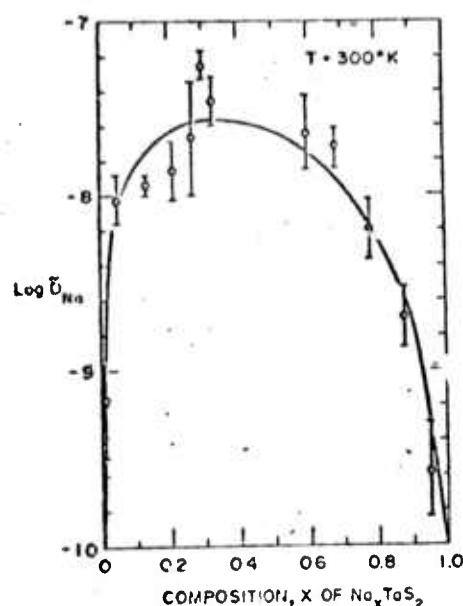


Figure 5: Measured dependence of $\log \bar{D}_{Na}$ with composition x in Na_xTaS_2 at $300^\circ K$. Solid line is fitted curve of $\log \bar{D}_{Na} = \log (\text{constant}) + \log [x(1-x)^2]$.

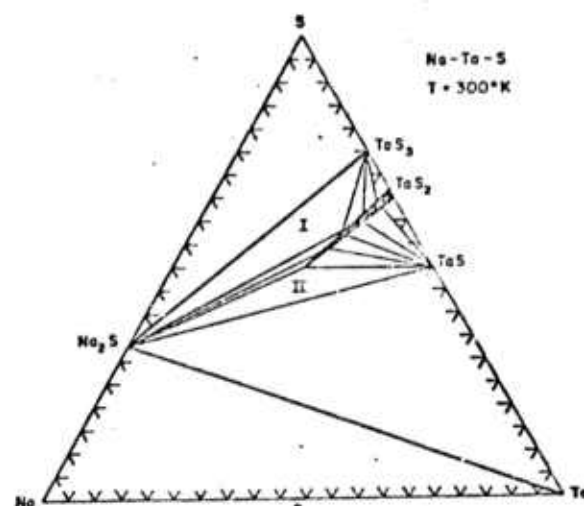
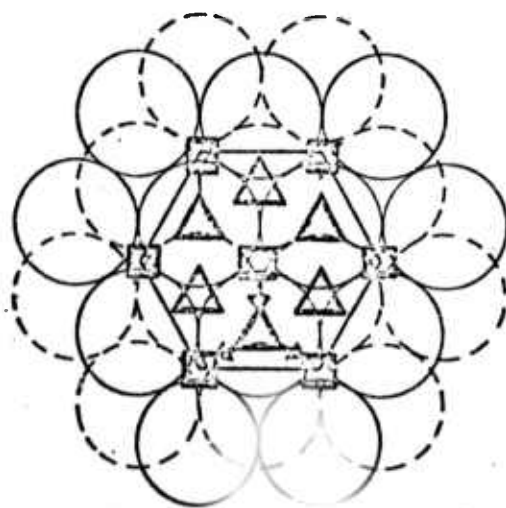


Figure 6: Proposed Isothermal ternary section for the Na-Ta-S system at $300^\circ K$.



□ OCTAHEDRAL SITE
Δ TETRAHEDRAL SITE

Figure 7: Schematic picture of tetrahedral (Δ) and octahedral (\square) sites for sodium in the van der Waals gaps of Na_xTaS_2 . The broken lines indicate the sulfur atoms below the gap; the solid lines indicate sulfur atoms above the gap. Arrows indicate the proposed diffusion path, i.e., octahedral \rightarrow tetrahedral \rightarrow octahedral.

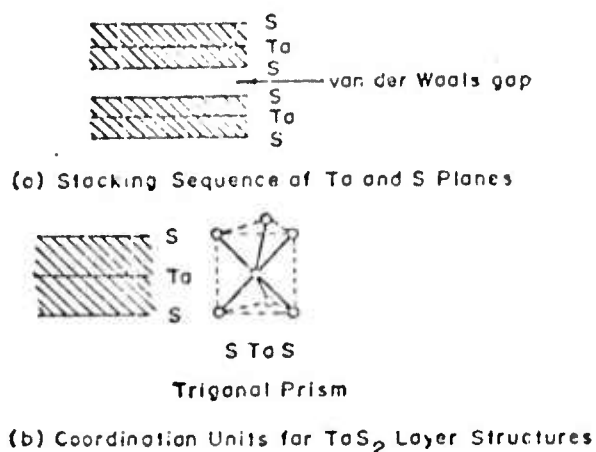


Figure 1: Structural characteristics of 2H-TaS_2 .

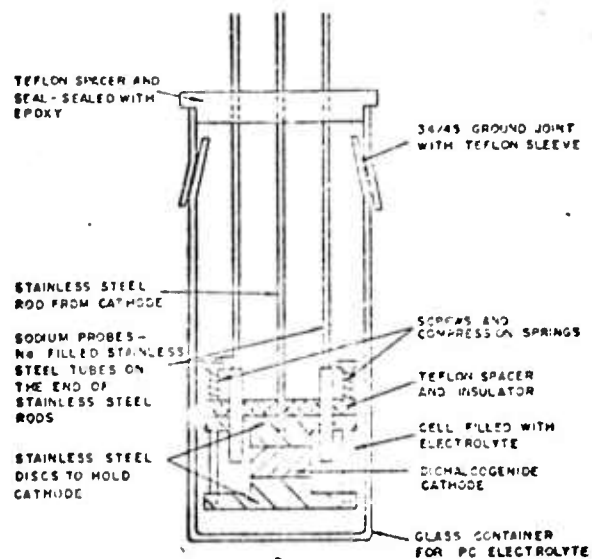


Figure 2: Experimental cell.

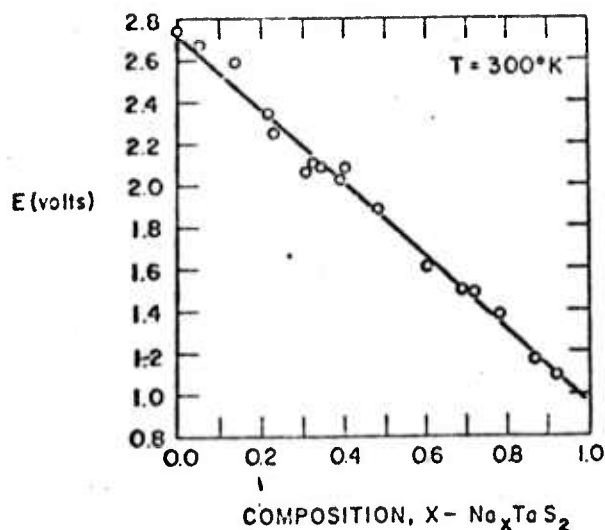


Figure 3: Measured cell voltage as a function of composition x in Na_xTaS_2 at 300°K .

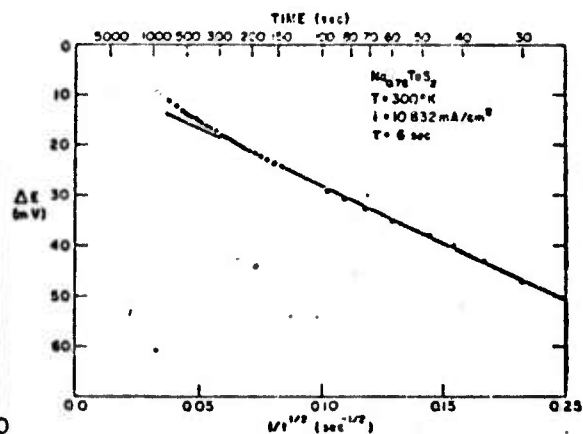


Figure 4: Typical experimental curve of ΔE vs $(\text{time})^{-1/2}$.

To appear in "Electrode Materials and Processes for Energy Conversion and Storage", J. D. E. McIntyre, S. Srinivason and F. G. Will eds., The Electrochemical Society, Princeton, N.J. (1977).

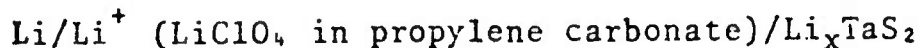
ELECTROCHEMICAL DETERMINATION OF THE CHEMICAL
POTENTIAL OF LITHIUM IN Li_xTaS_2 AT 300°K

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ABSTRACT

Tantalum disulfide intercalated with lithium offers exciting possibilities as a novel electrode material. The thermodynamic properties of lithium in Li_xTaS_2 where x varies from 0 to 1.0 have been determined using electrochemical cell techniques. The electrochemical cell is:

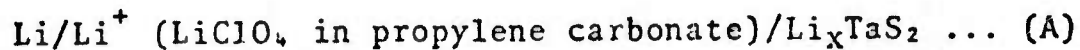


Such thermodynamic data are necessary not only to understand chemical bonding in these intercalated materials but also to quantitatively assess their specific applications as cathodes in secondary alkali-metal battery systems.

INTRODUCTION

The dichalcogenides of transition metals have received considerable attention in recent years because of their unique properties. These dichalcogenides form layered compounds in which layers of metal, M, are sandwiched between layers of anion, X, in a hexagonal symmetry. A van der Waals gap exists between the anion layers as shown in Fig. 1 for TaS_2 in its 2H polymorph (1). Alkali metals like Li, Na, and K are known to intercalate readily within the van der Waals gaps in these structures (2,3,4).

For alkali-metal based battery systems, one needs a cathode material having a very low chemical potential of the alkali metal over a wide composition range. The chemical potential and diffusivity of lithium in Li_xTaS_2 , where x varies between 0 to 1.0, are being determined over the entire range of composition. Such fundamental data are essential for the assessment of the suitability of Li_xTaS_2 as a cathode material in lithium batteries. The electrochemical cell used for our investigation is:



This paper reports the electrochemical determination of chemical potential of lithium in Li_xTaS_2 as a function of composition.

EXPERIMENTAL

Tantalum disulfide (typically 99.8%) was obtained from CERAC. This material was found to consist of several other phases apart from the 2H-polytype. The Ta:S ratio of the material was more than 1:2. The 2H-polytype of TaS_2 was prepared by annealing the material at 580°C under a flow of purified argon and in presence of sulfur at $200\text{--}300^\circ\text{C}$ for 7 days. X-ray investigation of the annealed tantalum disulfide revealed that conversion to 2H-polytype was complete. The 'a' and 'c' parameters of annealed 2H- TaS_2 were determined to be 3.312 and 12.08 respectively and were in fair agreement with literature values (2,3).

Solution of n-butyl lithium (2.2 molar) in hexane (from Ventron) was used after 1:3 dilution to intercalate (5) lithium in 2H- TaS_2 inside a controlled atmosphere box ($\sim 1\text{ ppm}$ moisture) with argon-5% hydrogen environment. Powders of TaS_2 were immersed in a known volume of diluted n-butyl lithium solution for about 2-4 days, although the intercalation process is essentially completed within one day. The intercalating solutions were separated by filtration. The solids were washed repeatedly with hexane, vacuum dried and stored in stoppered bottles inside a controlled-atmosphere box. The composition of intercalated compounds, Li_xTaS_2 , was determined by the analysis of initial and final lithium content of the intercalating solutions. The analysis was carried out by titration with standardized ($\frac{N}{10}$) HCl.

The as-received propylene carbonate (99% Aldrich) was found to contain ~ 200 ppm moisture when analyzed in a Perkin-Elmer gas chromatograph. In order to remove this moisture, propylene carbonate was mixed with small chips of freshly cut lithium metal (Ventron, 99.9%) in a bottle, and the mixture was agitated in a laboratory shaker for about 7 days. The mixture turned grey and clear moisture-free propylene carbonate was separated from solids by filtration inside the controlled atmosphere box.

Anhydrous LiClO_4 (Ventron, 99.5%) was dried under vacuum (10μ) at 150°C for one day. The dried LiClO_4 was dissolved in propylene carbonate in concentrations around 1.0 molar to prepare the electrolyte.

Fig. 2 shows schematically the experimental cell. Cathode pellets of Li_xTaS_2 were prepared by isostatically pressing powders at $\sim 85,000$ psi. Initial attempts to compact

Li_xTaS_2 powders in an ordinary die press produced preferentially oriented pellets, where the c-axis of the Li_xTaS_2 lattice was aligned along the axis of loading. These preferentially oriented pellets disintegrated easily when a current was passed through the cell. The lithium content of the Li_xTaS_2 cathode changes with current flow. This variation can develop internal stresses in the Li_xTaS_2 lattice due to changes in the c-parameter of the lattice. Isostatically pressed pellets of Li_xTaS_2 required grinding and polishing in order to fit into the cathode holder. The typical weight of a cathode pellet was 0.3 g. The anode was freshly cut lithium. Argon, which was purified by passing successively through dryrite, molecular sieve and a titanium-chip getter at 550°C, passed over the cell. If the cell voltage was stable ($\pm 0.5\text{mv}$) for 2-3 days, then it was recorded using a Kithley model 630 electrometer. In some cases the composition of Li_xTaS_2 was changed by passing a constant current of 50 μA through the cell using a Tacussel PIT 20-2X potentiostat. Most of the cells were operated at $\sim 30^\circ\text{C}$ and two were operated $\sim 70^\circ\text{C}$. Cells were not operated at temperatures higher than 70°C because of the possibility of dissociation of propylene carbonate of the cell electrolyte (6,7).

RESULTS AND DISCUSSION

Fig. 3 shows the voltage of the cell (A) as a function of composition, x , of Li_xTaS_2 for various cells. The variation of cell voltage (E) with composition, x , of Li_xTaS_2 can be described by a straight line of equation:

$$E = 2.92 - 1.46x \quad \dots (1)$$

The chemical potential of lithium, μ_{Li} , at any composition is given by:

$$\mu_{\text{Li}} = -nF \cdot E = -F(2.92 - 1.46x) \quad \dots (2)$$

As shown in Fig. 3, temperature does not have a pronounced influence on cell voltage. The linear variation of cell voltage with composition in alkali-metal intercalated transition metal disulfide has also been observed in Na_xTaS_2 (8). However, non-linear variations of cell voltage in Na_xTiS_2 (9) and Li_xTiS_2 (19) have been observed. The linear variation of cell voltage observed in our system indicates that the cathode remained single phase throughout the composition range. The chemical potential of lithium in Li_xTaS_2 calculated from Eq. (2) varied from -64.0 to -33.61 K-cal/g. atom corresponding to a value of $x = 0.1$ and $x = 1.0$ respectively.

The free energy of formation of the compound Li_xTaS_2 may be represented (8) as:

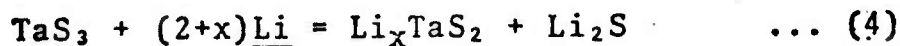
$$\Delta G^{\circ}_f(\text{Li}_x\text{TaS}_2) = \Delta G^{\circ}_f(\text{TaS}_2) - nF \int_0^x (2.92 - 1.46x) dx \dots (3)$$

Larson and Elliott (11) determined the free energy of formation of TaS_2 in 850-1100°C temperature range. Extrapolation of their data to 300°K gives a $\Delta G^{\circ}_f(\text{TaS}_2) = -70.5 \pm 3$ K-cal per mole with reference to pure solid sulfur as standard state. Using this value, and setting $x = 1$ in Eq.(3) a value of -121.0 ± 3.0 K-cal/mole is obtained for $G^{\circ}_f(\text{LiTaS}_2)$.

All free energy values quoted in this paper are based on solid sulfur as the standard state. The difference between solid sulfur and gaseous sulfur standard state is $+9.5$ K-cal/g-atom of sulfur at 300°K. The free energy values determined by the present investigation for Li_xTaS_2 can be correlated with known phase relationships in the ternary Ta-S-Li system. Fig. 4 shows the isothermal section of ternary Ta-S-Li system at 300°K considering only Li_2S , TaS_3 , TaS_2 and TaS as the stable binary phases. The point A represents the saturated intercalation compound LiTaS_2 .

Although there is no thermodynamic data for TaS_3 , its thermodynamic stability must be between $\Delta G^{\circ}_{\text{TaS}_2}$ and $1.5 \Delta G^{\circ}_{\text{TaS}}$ (8,10). If we assume TaS_3 to be slightly more stable than TaS_2 , a value of -75 K-cal/mole is reasonable for $\Delta G^{\circ}_{\text{TaS}_3}$ (8).

In the upper portion of the ternary diagram, Li_xTaS_2 is expected to be in equilibrium with Li_2S and TaS_3 . We can estimate the exact composition of Li_xTaS_2 in equilibrium with TaS_3 and Li_2S by considering the following equilibrium:



Thus

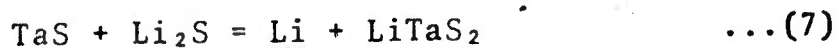
$$(2+x)\mu_{\text{Li}} + \Delta G^{\circ}_f(\text{TaS}_3) = \Delta G^{\circ}_f(\text{Li}_x\text{TaS}_2) + \Delta G^{\circ}_f(\text{Li}_2\text{S}) \dots (5)$$

Where, μ_{Li} is given by Eq.(2), $\Delta G^{\circ}_f(\text{Li}_x\text{TaS}_2)$ is given by Eq. (3) and $\Delta G^{\circ}_f(\text{TaS}_3) = -75$ K-cal/mole. Juza and Uphoff (12) reported the heat of formation of Li_2S at 298°K as -106.7 K-cal/mole. Freeman (13) estimated the standard entropy, S°_{298} for $\text{Li}_2\text{S} = 14 \pm 3$ cal/°K/mole. Using the standard entropy values (14) of 6.954 and 7.631 cal/mole/°K for lithium and sulfur, $\Delta G^{\circ}_f(\text{Li}_2\text{S})$ is calculated to be -104.45 K-cal/mole at 298°K. Substitution of all these free energy values in Eq. (5) yields a quadratic equation in composition x :

$$0.7285x^2 + 2.914x - 1.508 = 0 \quad \dots(6)$$

Eq. (6) yields a value of 0.46 for x as shown in the upper three phase triangle indicated in Fig. 4. Of course, the calculated equilibrium composition of Li_xTaS_2 in this three phase triangle depends on the selected value for the free energy formation of TaS_3 .

Jellinek (15,16) did not observe a TaS phase in the phase identification work on Ta-S binary system in the 600-1000°C temperature range. However, Biltz and Köcher (17) reported a subsulfide TaS_{1-x} (where $0 < x < 0.7$). In the analogous Nb-S system, monosulfide NbS is a stable phase below 800°C (18). Assuming that TaS is a stable phase at 300°K, we can estimate its thermodynamic stability by considering the following equilibrium in the Ta-S-Li system:



Thus

$$\Delta G^\circ_f(\text{TaS}) = \Delta G^\circ_f(\text{LiTaS}_2) + \mu_{\text{Li}} - \Delta G^\circ_f(\text{Li}_2\text{S}) \quad \dots(8)$$

Where μ_{Li} is given by Eq. (2), $\Delta G^\circ_f(\text{Li}_2\text{S})$ and $\Delta G^\circ_f(\text{LiTaS}_2)$ are -104.45K-cal/mole and -121.0K-cal/mole respectively. We obtain $\Delta G^\circ_f(\text{TaS}) = -50.2 \pm 3\text{K-cal/mole}$ at 300°K. In a thermodynamic analysis of the Ta-S-Na system, Nagelberg and Worrell (8) calculated $\Delta G^\circ_f(\text{TaS}) = -47.9 \pm 3\text{K-cal/mole}$, which is in good agreement with the value obtained from Eq. (8).

If TaS is assumed to be unstable, then the three phase equilibrium on the lower side of Li_xTaS_2 would involve Li_2S , LiTaS_2 and tantalum. The solid solubility of sulfur and lithium in tantalum is negligible and the chemical potential of tantalum μ_{Ta} should essentially be zero. However, the Li_2S - LiTaS_2 -Ta equilibrium requires that the μ_{Ta} be -13.3K-cal/g.atom. Thus the three phase thermodynamic analysis leads to an unacceptable value for μ_{Ta} .

In our current experiments the diffusivity of lithium in Li_xTaS_2 is being determined as a function of composition x . Studies of the behavior of Li_xTaS_2 with other electrolytes like Li^+ - Na^+ beta aluminas and LiCl - KCl fused salts are also under way.

SUMMARY

Lithium intercalates in 2H-TaS_2 as Li_xTaS_2 over a wide range of composition ($0 < x < 1$). The voltage of the cell using Li_xTaS_2 as cathode against pure lithium anode varies between 2.92 to 1.46 volts depending on the composition x .

The measured values of the chemical potentials of lithium in Li_xTaS_2 have been used in a thermodynamic analysis of the equilibrium-phase relationship in Ta-S-Li system at 300°K.

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REFERENCES

- 1) J. A. Wilson and A. D. Joffe, Adv. in Physics, 18, p. 193 (1969).
- 2) M. S. Whittingham and F. R. Gamble, Mat. Res. Bull., 10, p. 363 (1975).
- 3) D. W. Murphy, F. J. Disalvo, G. W. Hull, and J. V. Waszczak, Inorg. Chem., 15, p. 17 (1976).
- 4) W.P.F.A.M. Omloo and F. Jellinek, J. Less. Comm. Met. 20, p. 121 (1970).
- 5) M. B. Dines, Met. Res. Bull., 10, p. 287 (1975).
- 6) A. N. Dey and B. P. Sullivan, J. Electrochem. Soc., 117, p. 222 (1970).
- 7) R. J. Jasinski and S. Kirkland, Anal. Chem., 39, p. 1663 (1967).
- 8) A. S. Nagelberg and W. L. Worrell, Proc. of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage, Electrochem. Soc., Philadelphia (1977).
- 9) D. A. Winn, J. M. Shemilt, and B. C. H. Steele, Mat. Res. Bull., 11, p. 559 (1976).
- 10) W. L. Worrell and A. S. Nagelberg, Symp. and Workshop on Adv. Battery Res. and Design, Argonne National Laboratory Report ANL-76-8, p. B-2 (1976).
- 11) H. R. Larson and J. F. Elliott, Trans. Met. Soc. AIME, 239, p. 1713 (1967).
- 12) R. Juza and W. Uphoff, Z. Anorg. Chem., 287, p. 113 (1956).
- 13) R. Freeman, Thermodynamic Properties of Binary Sulfides, Oklahoma State Univ. Research Found. Rep. 60 (1962).